



Highly active and durable chemically ordered Pt–Fe–Co intermetallics as cathode catalysts of membrane–electrode assemblies in polymer electrolyte fuel cells

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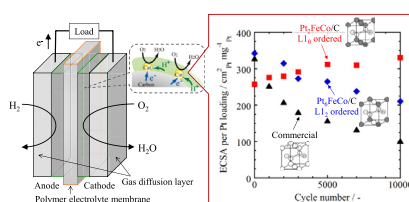
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HIGHLIGHTS

- Activity and durability of ordered intermetallics were compared with a commercial Pt/C.
- Ordered Pt–Fe–Co intermetallics showed higher mass activity in solution than Pt/C.
- ECSA of Pt₂FeCo/C was retained during durability test using MEA.
- The retention of ECSA was supported by smaller changes in the particle size.
- The chemically ordered structure was retained in Pt₂FeCo/C after durability tests.

GRAPHICAL ABSTRACT



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ABSTRACT

A cathode catalyst with enhanced activity for the oxygen reduction reaction and high durability is greatly required in polymer electrolyte fuel cells (PEFCs). We report that chemically ordered intermetallics, Pt₂FeCo/C with L1₀ ordered structure and Pt₆FeCo/C with L1₂ ordered structure, achieve both higher activity in solution and higher durability as the cathode catalyst of a membrane–electrode assembly (MEA) under actual PEFC operating conditions, compared with a commercial Pt/C. The mass activity of Pt₂FeCo/C is about twice as high as that of a commercial Pt/C, and Pt₆FeCo/C has a slightly higher mass activity than a commercial Pt/C in solution. These intermetallics were evaluated for durability as the cathodes of MEAs. During the load cycle durability test, the electrochemical surface area (ECSA) of Pt₂FeCo/C is retained, while that of Pt₆FeCo/C decreases, although less than a commercial Pt/C. The retention of ECSA is consistent with smaller changes in the particle size, observed with transmission electron microscopy, of the intermetallics than of a commercial Pt/C. X-ray diffraction patterns after the durability test show that while some part of ordered intermetallics is transformed into pure Pt, the chemically ordered structure of Pt₂FeCo/C is largely retained. Highly active and durable ordered intermetallics are promising as cathode catalysts of PEFCs.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are promising energy devices for residential and automotive applications. One of the important issues to be solved in PEFCs is the enhancement of the activity of the oxygen reduction reaction (ORR) at the cathode without sacrificing the durability of the catalyst [1,2]. To improve the ORR activity of platinum (Pt), various metals have been alloyed with Pt [3–22]. In particular, a Pt-enriched skin surface or a core–shell structure with a Pt-rich shell formed on these alloys has been reported to be effective in increasing the surface activity for ORR [3–10,14–17]. However, when less-noble metals are exposed on the surface, such metals can easily dissolve in the strong acidic conditions of PEFCs [1], which leads to a decrease in performance. Furthermore, Pt nanoparticles themselves degrade, or increase their size, due to potential cycling during the operation of PEFCs [23–25].

Leaching tolerance of less-noble metals in acidic solution has been reported in chemically ordered Pt-based intermetallic compounds such as Pt–bismuth (Bi) and Pt–tin (Sn) [26,27], in studies of the electrochemical oxidation of small organic molecules [28]. Recently, other Pt-based intermetallics, such as Pt–iron (Fe), Pt–cobalt (Co), and ternary Pt–Fe–Vanadium (V) and Pt–Fe–Co have been found to show both high activity for ORR and high durability, including in our previous research [29–33]. The intermetallics, Pt–Metal (M) with $L1_0$ ordered face-centered tetragonal structure (CuAu-type) and Pt_3M with $L1_2$ ordered structure (Cu₃Au-type) have been examined. Comparison between intermetallics and disordered alloys after potential cycling revealed that ORR activity of the former was better retained [29–33], and the electrochemical surface area (ECSA) of Pt either increased or was better retained [31–33]. Higher retention of ECSA was consistent with smaller changes in particle size distribution [33]. The high durability was ascribed to retention of the content of less-noble metals during immersion in acid solution [29] and of the ordered intermetallic structure during potential cycling in acid solution [32,33]. These results clearly show that the ordered intermetallics are promising candidates as ORR catalysts for PEFCs. However, these evaluations of their durability were performed in solution using the rotating disk electrode (RDE) technique, and thus the conditions were different from those of an actual PEFC whose core component is a membrane electrode assembly (MEA). The local environment around the catalyst in aqueous solution differs from that in an MEA. In an MEA, water is supplied in the gas phase and is sorbed into the polymer electrolyte that surrounds the catalyst. Furthermore, evaluations in solution are generally performed at lower temperature than the standard operating temperature of MEAs, which is around 80 °C. These differences between MEA and RDE result in differences in catalyst degradation [34]. Thus, catalysts that show high durability in acid solution should be evaluated using MEAs.

In the present study, we evaluated ordered Pt–Fe–Co intermetallics supported on carbon (C) and then compared them to a commercial catalyst in terms of their ORR activity in solution and their durability as cathode catalysts of an MEA. The ordered intermetallics evaluated were Pt_2FeCo with $L1_0$ ordered structure and Pt_6FeCo with $L1_2$ ordered structure. The commercial catalyst was supplied by Tanaka Kikinzoku Kogyo (TKK). The methodology used for evaluation of durability using MEA was a revised protocol for load cycle durability testing, which mainly accelerates Pt degradation [23,24], recommended by the Fuel Cell Commercialization Conference of Japan (FCCJ) [23]. The structures of the catalysts and the construction of MEAs, which were used for evaluation of durability of the catalysts, are schematically illustrated in Fig. 1.

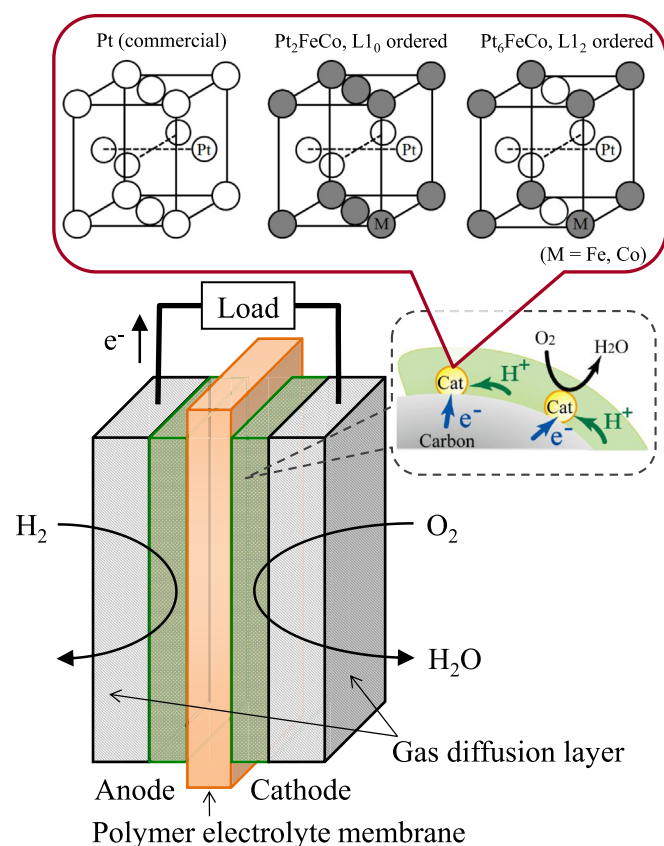


Fig. 1. Structures of the catalysts, Pt_2FeCo/C with $L1_0$ ordered structure, Pt_6FeCo/C with $L1_2$ ordered structure, and commercial Pt/C , and the construction of MEAs, which were used for evaluation of durability of the catalysts.

The change in ECSA and particle size distribution before and after the load cycle test showed that the ordered intermetallics had superior durability compared with the commercial catalyst under actual PEFC operating conditions.

2. Experimental

All the metallic precursors and chemicals used in this study were purchased from Wako Chemicals unless otherwise specified. Pt_2FeCo/C and Pt_6FeCo/C were synthesized using our previously reported procedure [33]. Briefly, metallic precursors, hexachloroplatinic acid, vinyl ferrocene, and cobalt acetate tetrahydrate were mixed with carbon black (Ketjen black), and ground well. The weight ratio between the metallic precursors was adjusted to the required metal atomic ratio in products, and the total amount of metallic precursors was set so that the metal content of the catalysts was 40 wt%. Then, an appropriate volume of isopropyl alcohol was added and the paste-like mixture ground

Table 1

Atomic composition and metal particle sizes of Pt_2FeCo/C , Pt_6FeCo/C , and TKK Pt/C before and after durability tests (10,000 cycles, using MEAs at 80 °C).

Catalyst	Atomic composition Pt:Fe:Co (molar ratio)	Metal particle size (mean \pm SD)/nm	
		Initial	After durability test
Pt_2FeCo/C	48:25:27	3.2 ± 1.3	3.8 ± 1.5
Pt_6FeCo/C	77:10:13	3.5 ± 1.1	4.4 ± 2.1
TKK Pt/C		3.2 ± 0.8	7.9 ± 4.6

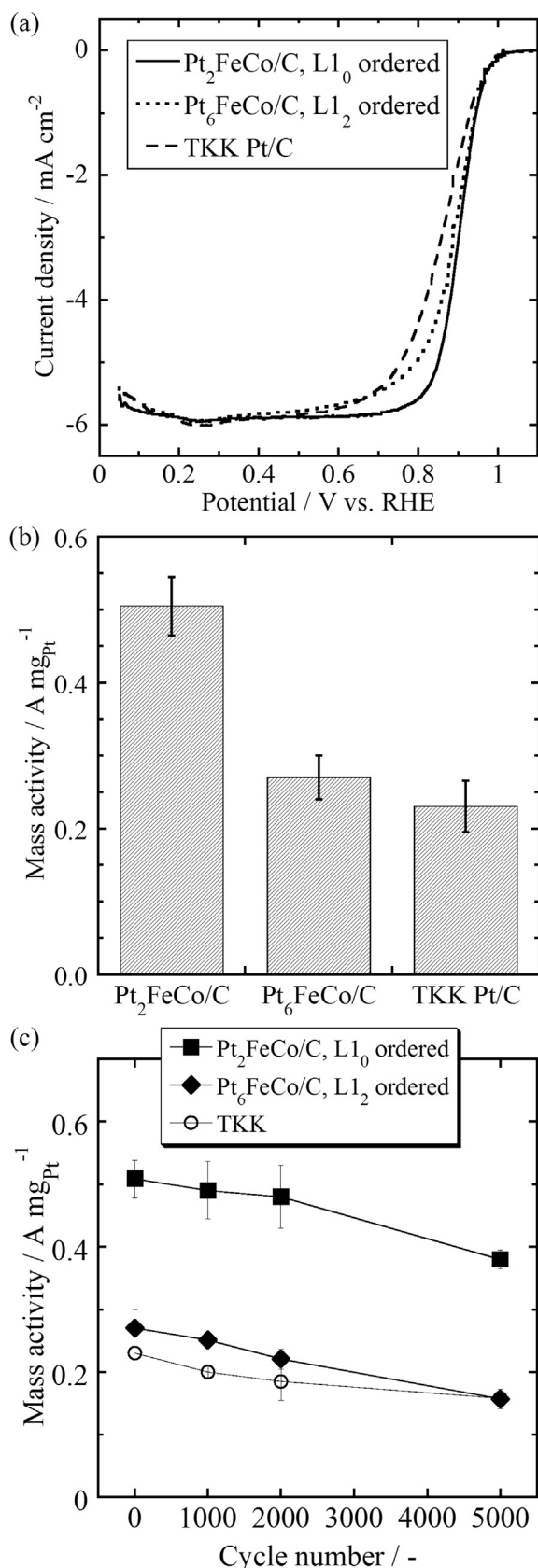


Fig. 2. (a) Polarization curves on RDE of Pt₂FeCo/C, Pt₆FeCo/C, and TKK Pt/C measured in O₂-saturated 0.1 M HClO₄ solution, (b) mass activities at 0.9 V, and (c) change in mass activities as a function of the number of cycles at room temperature; the durability test was performed in 0.1 M HClO₄ solution. The error bars denote the standard

deviation of three independent measurements. (Data on Pt₂FeCo/C and TKK Pt/C were reported previously [33].)

well. The mixture was then reduced in the presence of 20% H₂ with N₂ as carrier gas in a tube furnace for 4 h at 800 °C. The commercial catalyst used was TEC10E50E with 45.8 wt% Pt from TKK (TKK Pt/C). The catalyst composition was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) with an ICPS-8100 (Shimadzu) after dissolving the catalysts in aqua regia. Thermogravimetric analysis (TGA) was performed with a Pyris 1 TGA (PerkinElmer) to determine the total metal loadings. The values recorded were 47 and 48 wt% for Pt₂FeCo/C and Pt₆FeCo/C, respectively. The X-ray diffraction (XRD) data were measured with a RINT2000 (Rigaku) and a CuKα (λ = 1.5406 Å) X-ray source operating at 40 kV and 40 mA with a scanning rate of 2° min⁻¹. Transmission electron microscopy (TEM) was carried out using an H8100 electron microscope (Hitachi), with an accelerating voltage of 200 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and STEM-energy dispersive X-ray (STEM-EDX) line-scan measurements were performed using an HD-2700 C_s-corrected STEM (Hitachi High Technologies Corporation). ORR activity of the catalysts was evaluated in solution, using the RDE technique. The durability of these catalysts was first examined in acid solution, 0.1 M HClO₄, by applying square wave potential cycling: 0.6 V for 3 s and 1.0 V for 3 s. Preparation of the RDE and measurements were performed as reported previously [33]. All electrochemical measurements in solution using RDE were performed at room temperature.

Electrodes and MEAs were prepared as described in our previous study [35]. A Nafion solution (Aldrich, 5 wt% in a mixture of lower aliphatic alcohols and water), polytetrafluoroethylene (PTFE) suspension (Aldrich, 60 wt% in water), Vulcan XC72 carbon black (Cabot), and PTFE-treated carbon paper (ElectroChem) were used to fabricate the electrodes. Nafion NR-212 (DuPont) was used as the electrolyte membrane. The weight ratio of C of the catalysts to Nafion to PTFE was set to 32:25:15. Three catalysts, Pt₂FeCo/C, Pt₆FeCo/C, and TKK Pt/C, were used for the cathode. TKK Pt/C was used for all the anodes. The Pt loading in the cathode was 0.33 ± 0.07 mg cm⁻². The fabricated MEA was set in a 5 cm² single-cell test holder (ElectroChem).

The procedures for the load cycle durability test and cyclic voltammetry (CV) followed the revised protocols of FCCJ [23]. The measurements were performed at 80 °C and 100% relative humidity (RH), with flow rates of 100 mL min⁻¹ of H₂ for the anode and 500 mL min⁻¹ of N₂ for the cathode. The N₂ gas was stopped just prior to the CV measurements. The durability test was carried out by applying a rectangular wave between 0.6 and 1.0 V vs. reversible hydrogen electrode (RHE) with a holding time of 3 s at each potential value, 6 s for one cycle, using an automatic polarization system HZ-3000 (Hokuto Denko). CV measurements were performed with the potential sweep ranging from 0.05 to 0.9 V, at a sweep rate of 50 mV s⁻¹, using an automatic polarization system HZ-5000 (Hokuto Denko). Prior to the recording of measurements, CVs were performed several times until stable voltammograms were obtained. The performance of the MEAs was measured at 60 °C and 90% RH, with gas flow rates of 100 and 500 mL min⁻¹ for H₂ and O₂, respectively, using a charge–discharge unit HJ1010SM8A (Hokuto Denko). After carrying out the durability test, the cathode catalysts were evaluated using TEM, STEM-EDX, and XRD. The samples for TEM analysis were obtained by scratching the catalyst off the cathode layer. The samples for STEM-EDX analysis

were obtained by slicing the MEA into ultrathin samples. The samples for XRD analysis were prepared by removing the anode and the carbon paper.

3. Results and discussion

3.1. Properties of the catalysts and electrochemical characterization in solution using RDE

The atomic composition measured by ICP-AES and the metal particle size observed with TEM of the as-synthesized or received

(initial) catalysts are summarized in Table 1. XRD patterns of the catalysts are shown in Fig. S1. The patterns of Pt₂FeCo/C and Pt₆FeCo/C, especially the peaks that appear in the region lower than 40°, show the formation of chemically ordered L1₀ [31,33] and chemically ordered L1₂ [31,32] structures, respectively. The structure of Pt₂FeCo/C was further examined in our previous report [33]; existence of the ordered structure was confirmed by a selected-area electron diffraction (SAED) pattern with almost all the reflections corresponding to L1₀ type crystal structure and a very small degree of face-centered cubic (fcc) crystal, and by fast Fourier transform analysis of images taken by HAADF-STEM; the STEM-EDX line-scans showed that no clear core–shell structure was formed, although the Pt composition was rich near the particle surface. Fig. 2 shows the polarization curves of the catalysts on RDE (a), mass activities (I_m) of the catalyst at 0.9 V (b), and changes in I_m as a function of the number of potential cycles (c), measured in O₂-saturated 0.1 M HClO₄ solution at room temperature. The data on Pt₂FeCo/C and TKK Pt/C were reported previously [33]. The initial I_m value of Pt₂FeCo/C is about twice as high as that of TKK Pt/C, and Pt₆FeCo/C shows a slightly higher I_m than TKK Pt/C in solution. The higher I_m of Pt₂FeCo/C is retained after 5000 cycles of potential cycling in acid solution, as shown in Fig. 2(c).

3.2. Evaluation of durability of the catalysts using MEA

The ordered Pt–Fe–Co intermetallics with the high ORR activity were then evaluated for durability as the cathodes of MEAs. The results reported here were obtained using MEAs, unless otherwise stated. Fig. S2 shows current–voltage (I – V) curves at 60 °C using TKK Pt/C, Pt₂FeCo/C, and Pt₆FeCo/C as the cathode catalysts. Similar performances are observed for the MEAs using all three catalysts. The I – V curves of MEAs are affected not only by ORR activity, but also by structural parameters of catalyst layers, such as catalyst utilization that affects the performance even in a low-current-density region. In addition, the structure of the catalyst layers using ordered intermetallics fabricated in this study has not yet been optimized. Therefore, the order of the I – V curves differs from the order of catalytic activity measured in acid solution. To evaluate the ORR activity from I – V curves, the procedures used to fabricate catalyst layers using ordered intermetallics should be examined more carefully. Furthermore, the performance of MEAs should be

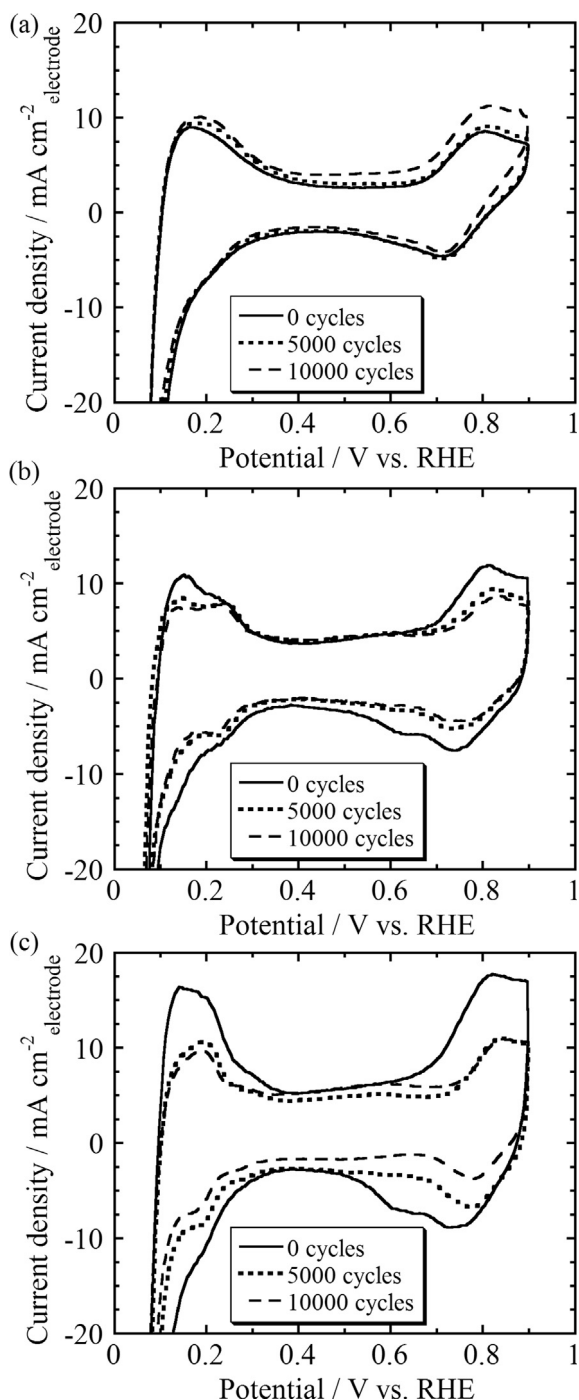


Fig. 3. CVs of (a) Pt₂FeCo/C, (b) Pt₆FeCo/C, and (c) TKK Pt/C during the load cycle durability test, using MEAs at 80 °C.

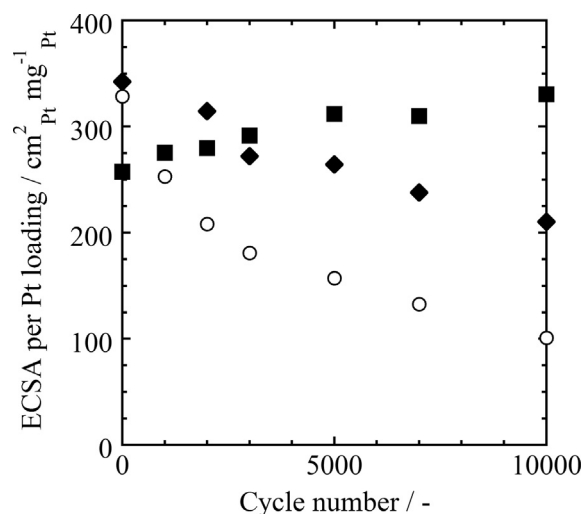


Fig. 4. Change in ECSA of Pt₂FeCo/C (solid square), Pt₆FeCo/C (solid diamond), and TKK Pt/C (open circle) per amount of Pt loading as a function of the number of cycles, using MEAs at 80 °C. The plots for Pt₂FeCo/C represent the average of two experiments.

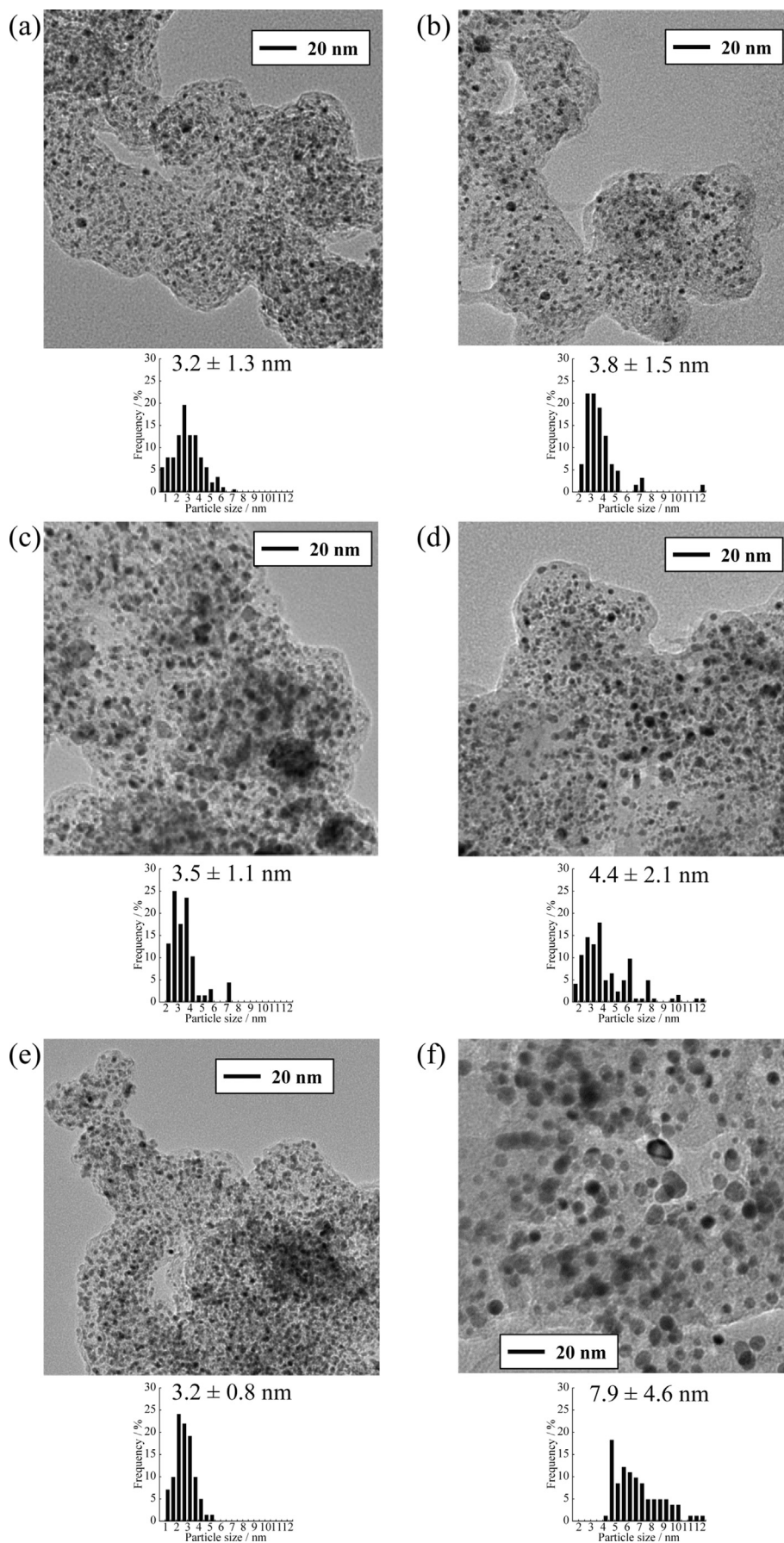


Fig. 5. TEM images of (a, b) Pt₂FeCo/C, (c, d) Pt₆FeCo/C, and (e, f) TKK Pt/C. The images (a, c, e) are initial, and (b, d, f) are after 10,000 cycles, using MEAs at 80 °C. Histograms of the particle size distribution are shown below each image. The numbers shown above the histograms are mean \pm standard deviation (SD) of the particle size.

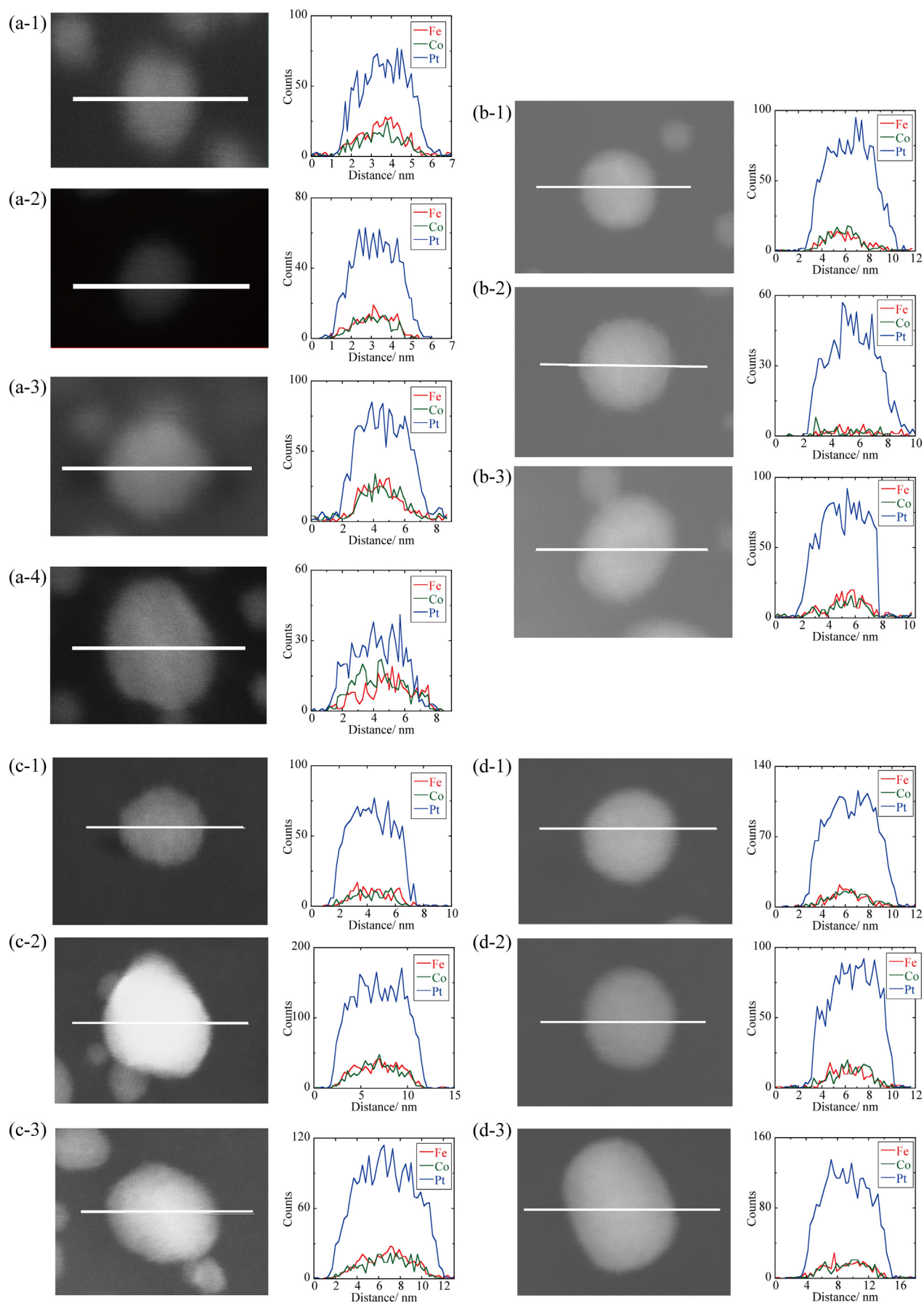


Fig. 6. HAADF-STEM images (left) and STEM-EDX line-scans (right) of (a and b) Pt₃FeCo/C and (c and d) Pt₂FeCo/C for three or four individual particles. The images (a and c) are initial, and (b and d) are after 10,000 cycles, using MEAs at 80 °C. (The images of initial Pt₂FeCo/C (a) were reported previously [33].).

Table 2

Average ratios of counts of Fe or Co to Pt around the center of the particles before and after durability tests (10,000 cycles, using MEAs at 80 °C).

Catalyst	Fe/Pt		Co/Pt	
	Initial	After durability test	Initial	After durability test
Pt ₂ FeCo/C	0.31 ± 0.06	0.11 ± 0.06	0.31 ± 0.14	0.11 ± 0.06
Pt ₆ FeCo/C	0.19 ± 0.03	0.13 ± 0.01	0.16 ± 0.04	0.14 ± 0.02

measured under standardized conditions. Our aim for using MEAs was to evaluate the durability, especially Pt degradation, of the catalysts under PEFC operating conditions.

The load cycle durability test at 80 °C was applied to MEAs. Fig. S3 shows *I*–*V* curves using TKK Pt/C and Pt₂FeCo/C as the cathode catalysts before and after the durability test. The differences in *I*–*V* curves are not significant; the similar trend with small change in *I*–*V* curves before and after the load cycle durability testing was reported previously for TKK Pt/C [24]. CVs obtained before the durability test (0 cycles), and after 5000 and 10,000 cycles at 80 °C are shown in Fig. 3(a–c). ECSA was calculated from the peak area of hydrogen desorption, by assuming the charge for removing a monolayer hydrogen on Pt to be 210 μC cm^{−2}. Fig. 4 shows the change in ECSA per amount of Pt loading as a function of the number of cycles. ECSA of Pt₂FeCo/C with L1₀ ordered structure is retained, or even increases slightly, during the durability test at least up to the 10,000 cycles performed in this study. The slight increase in ECSA during potential cycling was also reported previously in the evaluation of Pt–M in solution [31–33]. The possible reason is that leaching of less-noble metals near the surface exposed further Pt [32] or caused surface roughening. A similar reason for the slight increase in ECSA of L1₀ Pt₂FeCo/C may apply. Although ECSA of Pt₆FeCo/C decreases with the increase in the number of cycles, the decrease was smaller than that of TKK Pt/C; the ratio of ECSA after 10,000 cycles to the initial value is about 60% for Pt₆FeCo/C, while the ratio is about 30% for TKK Pt/C. The reason for the higher durability of L1₀ ordered Pt₂FeCo/C than L1₂ ordered Pt₆FeCo/C is unclear at this stage. However, there are several possible explanations: some differences may exist in the degree of formation of ordered structures, in the resistance to dissolution of less-noble metals from L1₀ and L1₂ ordered structures, and in structures after dissolution of less-noble metals from the particles. Further studies need to be performed to clarify the reason for these differences. The superior durability of ordered intermetallics, Pt₂FeCo/C and Pt₆FeCo/C, compared with TKK Pt/C

was further examined using TEM. Fig. 5 shows TEM images of the catalysts initially and after 10,000 cycles of the durability test, together with the particle size distribution. A large increase in particle size is observed in TKK Pt/C, while the change in the particle size is small for Pt₂FeCo/C and Pt₆FeCo/C, as summarized in Table 1. The smaller increase in the particle size in Pt₂FeCo/C and Pt₆FeCo/C is consistent with the retention of ECSA during the durability test.

After the durability test, the catalysts were evaluated using STEM-EDX and XRD. Fig. 6 shows the STEM-EDX line-scans of Pt₂FeCo/C and Pt₆FeCo/C, initially and after 10,000 cycles. Images of the initial Pt₂FeCo/C were reported previously [33]. Before and after the durability test, Fe, Co, and Pt are identified, with higher signals from Pt than from Fe and Co. To address the change in the atomic composition further, the average ratios of counts of Fe or Co to Pt around the center of the particles were calculated. The values are shown in Table 2. Although Fe and Co are found even after the durability test, the ratios of Fe/Pt and Co/Pt decrease after the durability test in both the catalysts, and the decrease is more in the case of Pt₂FeCo/C than Pt₆FeCo/C. These results show that some Fe and Co dissolves from the particles, while Fe and Co remain after the durability test. Fig. 7 shows the comparison of XRD patterns of the catalysts, initially and after 10,000 cycles. In the pattern of Pt₂FeCo/C after the durability test, a peak around 40° appears next to the original peak found in the initial catalyst. The position of the new peak corresponds to that of pure Pt, indicating the transformation of some L1₀ ordered Pt₂FeCo to pure Pt. A similar trend, the transformation from ordered intermetallics to pure Pt in some part of the catalyst, is also found in Pt₆FeCo/C, with the appearance of a shoulder around 40°, and the disappearance of the peak around 33° corresponding to the (110) plane of Pt₆FeCo/C, as shown in Fig. 7(d). However, of greater importance, the original peak around 40° with the peak position higher than that of pure Pt, indicating the incorporation of Fe and Co into Pt, remains in both Pt₂FeCo/C and Pt₆FeCo/C. In addition, the peak around 33° corresponding to the ordered structure remains in Pt₂FeCo/C even after the durability test. These results show that the chemically ordered structure is maintained in Pt₂FeCo/C after 10,000 cycles of the durability test performed on the MEA. The retention of the chemically ordered structure with some transformation to Pt was also determined by the SAED pattern after the durability test of Pt₂FeCo/C performed in solution [33].

We therefore propose that Fe and Co may dissolve from the outer layers of the metal particle, leaving a Pt-rich surface.

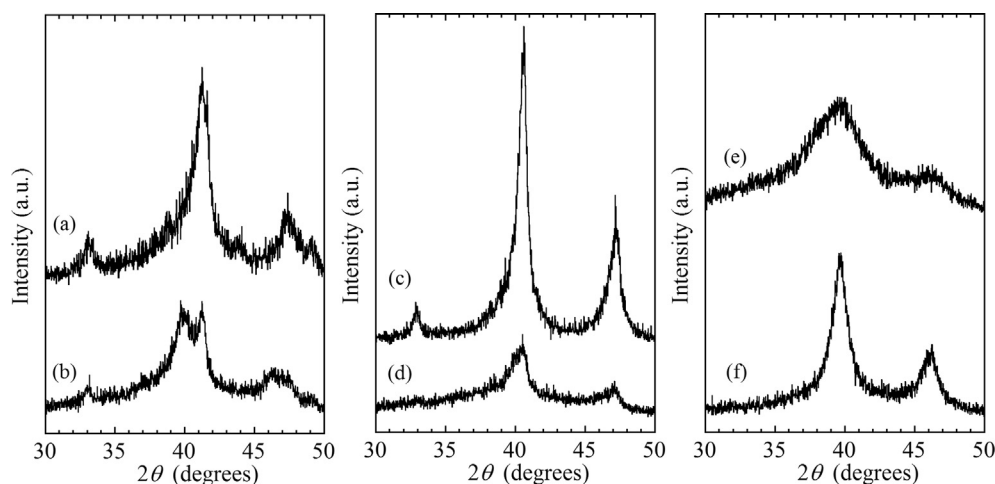


Fig. 7. XRD patterns of (a, b) Pt₂FeCo/C, (c, d) Pt₆FeCo/C, and (e, f) TKK Pt/C. The patterns (a, c, e) are initial, and (b, d, f) are after 10,000 cycles, using MEAs at 80 °C.

However, the dissolution of Pt, Fe, and Co may be retarded in the core of the particles with L1₀ ordered structure, leading to the retention of the chemically ordered structure found in Pt₂FeCo/C, and the retention of ECSA and the particle size. In previous studies, the more negative heat of formation for ordered intermetallics than for disordered alloys [36] is given as the reason for the high stability of ordered intermetallics compared with disordered alloys [28]. It was also shown that the enthalpy of formation of ordered intermetallics alone cannot explain the leaching tolerance of some less-noble metals [26]. The mechanism of the high durability of chemically ordered intermetallics is still unknown and thus should be addressed in future studies.

4. Conclusions

Ordered intermetallics, Pt₂FeCo/C with L1₀ ordered structure and Pt₆FeCo/C with L1₂ ordered structure, were evaluated for their ORR activity in solution and durability as the cathode catalyst of MEAs, and then compared with the commercial TKK Pt/C. The mass activity of Pt₂FeCo/C was about twice as high as that of TKK Pt/C, and Pt₆FeCo/C had slightly higher mass activity than TKK Pt/C in solution. The ordered Pt–Fe–Co intermetallics with high ORR activity were then evaluated regarding their durability as the cathodes of MEAs. ECSA of Pt₂FeCo/C was retained, or even increased slightly, during the durability test, while that of Pt₆FeCo/C decreased, but by less than TKK Pt/C. The retention of ECSA was consistent with the smaller change in the particle size observed for Pt₂FeCo/C and Pt₆FeCo/C than for TKK Pt/C. Although some part of the ordered intermetallics was transformed into pure Pt, the chemically ordered structure of much of Pt₂FeCo/C was retained.

This study shows that both higher activity in solution and superior durability under actual PEFC operating conditions were achieved by the chemically ordered intermetallics Pt₂FeCo/C and Pt₆FeCo/C, compared with the commercial TKK Pt/C.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.08.005>.

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